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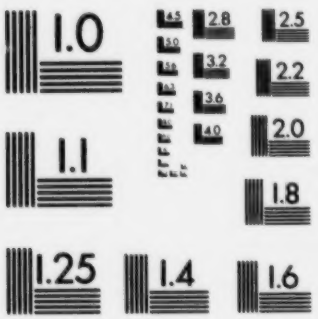

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ASSAY METHODS USED IN CANMET FOR THE DETERMINATION OF PRECIOUS METALS

P. E. MOLOUGHNEY
MINERAL SCIENCES LABORATORIES
CANMET

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ASSAY METHODS USED IN CANMET FOR THE DETERMINATION OF PRECIOUS METALS

P.E. Moloughney

PREFACE

A special analytical unit known as the Fire Assay Laboratory has existed for many years in CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch) for the determination of gold, silver, and the platinum group metals in diverse products.

Until the late 1950's the laboratory was limited mainly to the determination of gold and silver by the classical lead collection-cupellation assay procedure. However, in the late 1960's and 1970's, the advent of atomic-absorption spectrophotometry (AAS) and the analytical development of the tin-collection scheme of fire assay for the platinum group metals led to an appreciable expansion of the laboratory capabilities. At the same time the diversity of materials submitted for analysis also expanded greatly.

Fire assay texts discussing the traditional assay procedures published several decades ago are often still held in technical libraries; unfortunately, such texts are now difficult to obtain commercially. More recently developed analytical methods and schemes of analysis appear in the open literature; however, a collection of these methods together with the various assay procedures have never been made available in a convenient format.

In recent years, CANMET has received numerous requests from the public sector for detailed assay methods. These requests reflect a renewed active interest in Canada in gold and silver exploration and production, and arise because of the difficulties experienced in obtaining a working manual for precious metal analysis.

Therefore, to meet this need, the practical working details of the various assay methods used in CANMET laboratories have been collected in this manual. It will also be of use within CANMET for training personnel, and for assuring that procedural details of the various methods are not lost with the passage of time.

This manual is intended only as a procedural guide to the analyst; it is not a replacement for years of laboratory experience in fire-assaying. Guidance by an experienced analyst is essential when the manual is used by untrained personnel. Moreover, an extremely diverse range of materials is analyzed in

CANMET, and this manual does not attempt to cover every application or difficulty that could arise.

The manual not only contains methods for the determination of gold and silver in ores and metallurgical products by classical lead collection, but also includes the expansion of a gold-silver assay method to include platinum and palladium. In addition, a non fire-assay method is described for the determination of gold in cyanide solutions by solvent-extraction with methyl isobutyl ketone.

Some of the methods described in the manual have been applied to various reference materials certified for precious metals. The results obtained appear in the Appendix. They not only show the suitability of the methods for specific applications, but also indicate the precision and accuracy to be expected.

An analytical scheme for the determination of the platinum group metals and gold has been developed in CANMET. It is based on a pre-concentration of the precious metals by fire assay using tin as a collector, followed by chemical treatment of the resultant button. This scheme is partly described in Mines Branch Research Report R 154 published in 1965, and consequently is not included in the present manual.

MÉTHODES D'ESSAI UTILISÉES À CANMET POUR LA DÉTERMINATION DES MÉTAUX PRÉCIEUX

P.E. Moloughney

PRÉFACE

Il existe depuis un grand nombre d'années au CANMET (Centre canadien de la technologie des minéraux et de l'énergie, autrefois Direction des mines) une section spéciale d'analyse connue sous le nom de Laboratoire d'analyse pyrognostique, et chargée du dosage de l'or, de l'argent et des métaux du groupe de platine dans divers produits.

Jusqu'à la fin des années 1950, le laboratoire se contentait surtout d'analyser l'or et l'argent par le procédé classique de coupellation et d'extraction par le plomb. Toutefois, à la fin des années 1960 et 1970, l'introduction de la spectrophotométrie d'absorption atomique et la mise au point des procédés d'analyse pyrognostique consistant à recueillir avec de l'étain les métaux du groupe du platine ont permis une expansion notable des laboratoires. En même temps, la diversité des produits soumis à l'analyse a aussi grandement augmenté.

Les textes relatifs aux analyses pyrognostiques, dans lesquels sont décrits les procédés traditionnels d'analyse, et qui ont été publiés il y a plusieurs dizaines d'années, se trouvent souvent encore dans les bibliothèques techniques; malheureusement, il est maintenant difficile de les acheter. Dans la documentation accessible au public, on trouve une description des méthodes et schémas d'analyse plus récemment mis au point; toutefois, on n'a jamais pu trouver dans un format pratique un recueil de ces méthodes et en même temps des divers procédés d'analyse.

Depuis quelques années, le CANMET reçoit de nombreuses demandes du secteur public à propos de méthodes d'analyse détaillées. Ces demandes indiquent un renouvellement d'intérêt au Canada pour l'exploration des minerais d'or et d'argent et pour la production de ces métaux, et aussi les difficultés à obtenir un manuel pratique d'analyse des métaux précieux.

Par conséquent, pour répondre à ce besoin, on a réuni dans le présent manuel les détails pratiques des diverses méthodes d'analyses utilisées par les laboratoires du CANMET. Ce manuel permettra aussi au CANMET de former sur place son personnel, et évitera qu'on ne perde de l'information sur l'emploi des divers procédés, à mesure que passera le temps.

Ce manuel est seulement destiné à guider l'analyste; il ne peut se substituer à l'expérience acquise en analyse pyrognostique au cours d'années de travaux de laboratoire. Toute personne inexpérimentée utilisant ce guide doit aussi rechercher les conseils d'un analyste compétent. En outre, le CANMET analyse une très vaste gamme de produits, et ce manuel ne peut traiter de toutes les applications possibles ou de toutes les difficultés éventuelles.

Ce manuel décrit essentiellement les méthodes de détermination de l'or et de l'argent dans les minerais et les produits métallurgiques, par la méthode classique d'extraction en présence de plomb; il traite aussi d'une extension de la méthode d'analyse de l'or et de l'argent, permettant de doser en même temps le platine et le palladium. On y trouve de plus la description d'une méthode non pyrognostique de détermination de l'or dans les solutions cyanurées, par extraction avec le solvant méthylisobutylcétone.

Certaines des méthodes présentées dans le manuel ont été appliquées à divers produits de référence dont la teneur en métaux précieux a été certifiée. Les résultats obtenus sont indiqués en annexe; ils montrent l'applicabilité des méthodes dans des cas particuliers, et indiquent la précision et l'exactitude auxquels on peut s'attendre.

Le CANMET a mis au point une méthode analytique de détermination de l'or et des métaux du groupe du platine. Celle-ci consiste à effectuer une concentration préliminaire des métaux précieux par coupellation en présence d'étain, puis à soumettre au traitement chimique le bouton ainsi obtenu. Elle a été décrite en partie dans le rapport de recherche R 154 de la Direction des mines publié en 1965, et par conséquent ne figure pas dans ce manuel.

ACKNOWLEDGEMENT

The author wishes to thank J.C. Hole, Head, Ores and Fire Assay Section, Chemical Laboratory, CANMET, for his assistance and technical advice during the preparation of this manual.

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PRELIMINARY INFORMATION

BRIEF DESCRIPTION OF FIRE ASSAYING

The methods described in this manual involve the separation of precious metals from the sample matrix by a fire-assay fusion using lead collection. This classical method has been developed and refined over the years and is found in the early literature on the assaying of precious metals.

Fire assay consists essentially of three main parts: crucible fusion, cupellation, and parting. In addition, sample pretreatment, inquartation, and treatment of impure lead buttons are other important steps associated with it. These steps are outlined below and procedural details for each are given for each method.

A schematic outline of the procedure for the determination of gold and silver in a powdered sample by fire assay is shown in Figure 1.

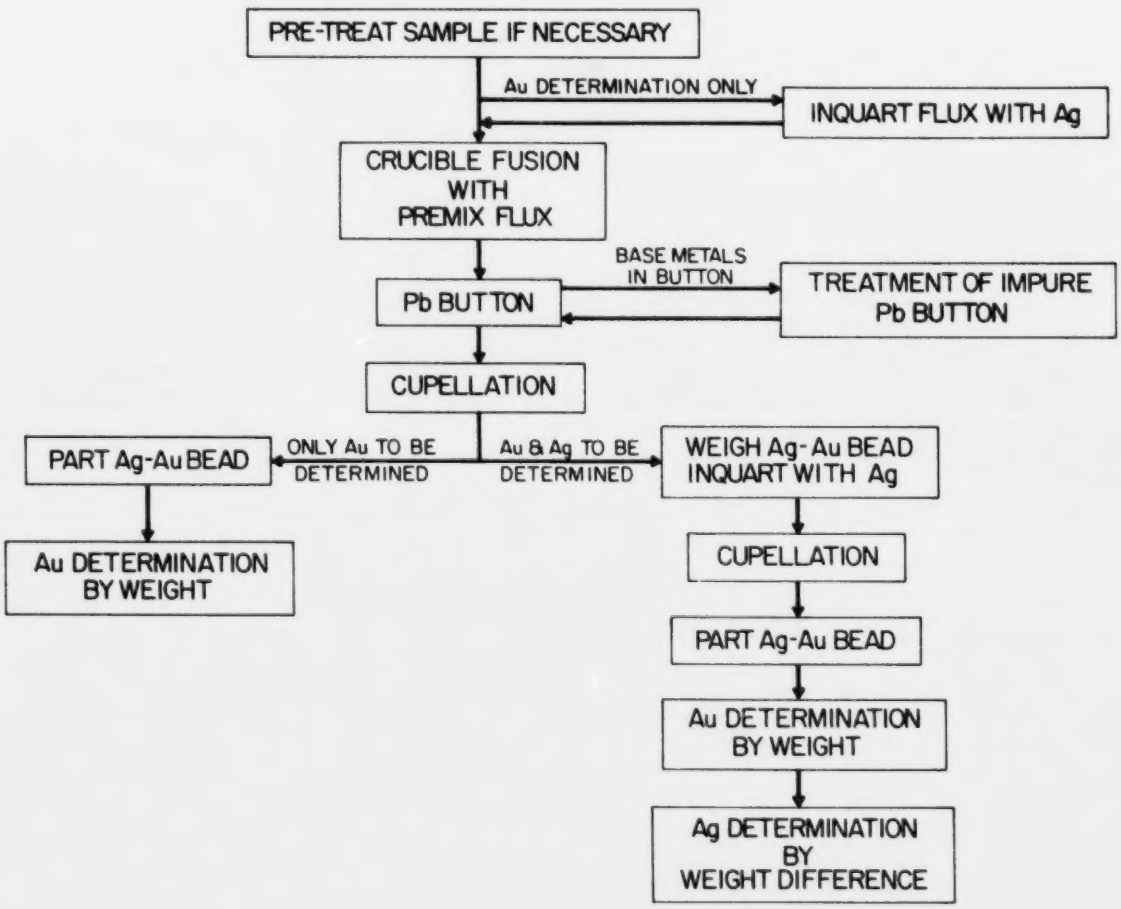

Figure 1. OUTLINE OF CLASSICAL FIRE ASSAY PROCEDURE

Crucible Fusion

For a crucible fusion, a sample is blended with varying amounts of flux materials and litharge (PbO), and the resulting mixture is transferred to a fire-clay crucible and is heated in the assay furnace. During fusion, a two-phase system, analogous to a conventional aqueous solvent extraction system, is formed. The impurities in the sample are oxidized by the flux and form a glassy slag; the litharge, in part, is reduced to fine particles of metallic lead that collect the precious metals while falling through the melt to separate from the slag phase as a lead button. The size of the lead button is controlled by controlling the oxidation-reduction reactions.

Cupellation

The lead button from the crucible fusion, containing the precious metals, is placed on a magnesia cupel and heated in the assay furnace. In this way, the lead is oxidized and the lead oxide is absorbed by the cupel. The resultant bead containing gold and silver is weighed to obtain the total precious metal content of the assay sample. If required, the bead is then inquarted with additional silver and re-cupeled (see Inquartation below).

Parting

The inquarted silver-gold bead obtained from the second cupellation step is treated with nitric acid to dissolve and remove the silver, and the remaining gold is weighed. The weight of silver is determined by difference.

Sample Pretreatment

Certain types of sample materials may require pretreatment before crucible fusion to remove or convert mineral constituents to a form that will not cause problems during fusion. Sulphur is converted to sulphate, or volatile oxides, as is arsenic. Chromite is pretreated by roasting with sodium peroxide, which converts the chromium to a form that enters the slag during crucible fusion.

Inquartation

To ensure complete parting of a silver-gold assay bead without breaking up of the gold, the silver-gold ratio of the bead must be adjusted by inquarting with additional silver. Usually a total of at least four to five times as much silver as gold is required to prevent breaking up of the gold (except when large quantities of gold are to be parted, as in the gold bullion assay, where a ratio of 2:1-3:1 is satisfactory).

If only gold is to be determined, silver is added to the assay charge before crucible fusion. If both gold and silver are to be determined, silver is added after the bead from cupellation is weighed; the bead and added silver are wrapped in lead foil and are re-cupeled.

When a gold determination is requested and the possible gold and silver concentrations are unknown, an arbitrarily chosen amount of up to 10 mg silver in the form of silver nitrate or foil is added to the assay charge before crucible fusion.

Treatment of Impure Lead Buttons

Lead buttons from the crucible fusion may be contaminated with large amounts of base metals; they are purified either by scorification, or by "soaking" in basic litharge slag.

Scorification involves heating the lead button with added lead in an open scorifying dish, and pouring the melt to separate the lead button from the slag containing the impurities. This process may be repeated if necessary.

Litharge soaking requires a second crucible fusion, in which the lead button is fused with a basic litharge slag. The melt is poured and the button separated as usual.

Apparatus

Only laboratory equipment required for the routine operation of the Fire Assay Laboratory is described here. Details of the preparation and use of special equipment will be given in the methods requiring its use.

- Assay furnace. A 15-Kw Globar furnace equipped with suitable thermocouple and temperature controller to maintain operating temperatures from 750°-1250°C.
- Assay crucibles. "30 gram" type.
- Assay scorifiers. 7.5 cm diameter.
- Roasting dishes. 11 cm diameter.
- Evaporating dishes. Coors porcelain No. 7 size.
- Annealing cups. 20-mL Coors porcelain.
- Cupels. Mabor magnesia, 3.8 cm diameter, capable of holding approximately 45 g of lead.
- Microbalance. Sensitivity 0.003 mg, total capacity 225 mg; used for weighing gold and silver assay beads.
- Pulp balance. Sensitivity 0.1 g, total capacity 800 g; used for weighing flux reagents and large sample portions for assay of ore and material of sub-ore grade.
- Analytical balance. Sensitivity 0.1 mg, total capacity 200 g; used for weighing samples rich in precious metals, and when only small quantities of material are available for assay.

REAGENTS

Only laboratory reagents required for the routine operation of the Fire Assay Laboratory are described here. Details of the preparation and use of special reagents will be given in the methods requiring their use.

- Parting solution. 25% and 50% vol/vol solutions of nitric acid in distilled water.
- Granulated test lead. Free of silver and gold.
- Lead foil. Free of silver and gold.
- Lead trays. 50-mL.
- Assay flux materials. Technical grade sodium carbonate, borax glass, silica, litharge, and flour. The litharge should be of the highest purity available, and free of silver and gold.

Standard Silver Solution

To prepare a standard silver solution, 100 µg/mL and 10 µg/mL in 10% vol/vol nitric acid dissolve 0.10 g of pure silver foil in 200 mL of 50% nitric acid, and dilute to 1 L with distilled water. Prepare a 10-µg/mL solution in 10% vol/vol nitric acid by diluting 10 mL of this stock solution and 9 mL of concentrated nitric acid to 100 mL with distilled water.

Standard Gold Solution

To prepare a standard gold solution, 100 µg/mL and 20 µg/mL in 10% vol/vol hydrochloric acid dissolve 0.10 g of Johnson-Matthey "Specpure" gold sponge in 25 mL of aqua regia; add 50 mg of sodium chloride to the solution to prevent formation of elemental gold during evaporation, and evaporate the solution slowly to near dryness. Dissolve the salts in 10 mL of concentrated hydrochloric acid and evaporate again to near dryness. Repeat the addition of hydrochloric acid and subsequent evaporation to remove most of the nitric acid. Dissolve the salts in 200 mL of 50% vol/vol hydrochloric acid and dilute to 1 L with distilled water. Prepare a 20 µg/mL solution in 10% vol/vol hydrochloric acid by diluting 20 mL of this stock solution and 8 mL of concentrated hydrochloric acid to 100 mL with distilled water.

Standard Palladium and Platinum Solutions

To prepare standard palladium and platinum solution, 100 µg/mL and 20 µg/mL in 10% vol/vol hydrochloric acid prepare each solution separately, in a manner similar to that described for the standard gold solution described above, using Johnson-Matthey "Specpure" sponge.

UNITS USED IN ASSAYING

In Canada, the United States, and South Africa, the assay result is traditionally expressed in troy ounces of precious metals per short ton (2000 avoirdupois pounds) of ore. A system of assay-ton weights is used for weighing the sample portion. The mass of 1 assay-ton is 29 1667 mg, which is the same as the number of troy ounces in a short ton. Therefore a precious metal concentration of 1 mg per assay-ton is equivalent to a concentration of 1 troy ounce per short ton.

In the SI system, precious metal concentration is expressed in parts per million (ppm) or its exact equivalent, micrograms per gram (µg/g). The relationship between the two systems is that 1 troy ounce per ton equals 34.3 µg/g.

In Australia and the United Kingdom the precious metal assay is commonly reported in pennyweights per ton.

The grain is an expression of precious metal weight occasionally encountered when describing coinage and jewellery.

Bullion assays for silver and gold are universally reported in millesimal fineness or parts per thousand. For example, sterling silver contains 92.5% silver and is reported as 925 fine.

The fineness of gold jewellery is reported in Karats (Kt) or twenty-fourth parts. For example, 24 Kt is pure gold, and 14 Kt is 58.3% gold or 583 fine. The term carat is occasionally used instead of Karat, but must not be confused with the carat used for diamonds and other precious stones.

The relationship between the units is as follows:

1 assay-ton	=	29.1667 grams (g)
1 troy ounce per ton	=	34.3 µg/g
1 troy ounce	=	31.1 g
	=	20 pennyweights (dwt)
	=	480 grains

ASSAY SAMPLE SIZE

Usually the analyst has some knowledge of the range of precious and base-metal values to be expected in the material for assay, and can choose a sample weight accordingly. The larger the sample taken, the more reliably it represents the parent material. Thus, for materials such as ores, rocks, and placer sands, that are known to be low in precious metals content, and may contain the minerals distributed unevenly throughout the material, 1- or 2-assay-ton samples should be taken for analysis. For metallurgical concentrates or high-grade material, 1/4- to 1/2-assay-ton samples are recommended. All material for assay should be ground to minus 100-200 mesh particle size prior to weighing the sample.

PRETREATMENT OF SAMPLES

Samples containing predominantly silica and metal oxides usually require no preliminary treatment; they may be mixed directly with the assay flux and fused. However, some form of pretreatment is necessary for samples high in sulphides and arsenides, those containing appreciable chromium, and those with a high content of lead sulphide.

Roasting of Sulphides and Arsenides

This process consists of heating the sample material in a furnace, and is often termed "calcining". In so doing, arsenides are decomposed and arsenic volatilized; similarly, sulphides are decomposed and sulphur is volatilized or converted to sulphate. By eliminating these constituents when present in a sample for assay, the formation of a matte or speiss during the subsequent crucible fusion is prevented.

In cases where only a few grams of material are to be roasted, place the weighed sample material on a bed of silica in a shallow fire-clay dish, and heat for about 1 h at 750-800°C. Remove the calcined material and proceed with the usual crucible fusion. The bed of silica serves to prevent any loss of the resultant calcine to the surface of the dish. Include the silica as part of that required for the assay charge.

Leaching of Copper-Nickel Matte

Because of the high copper-nickel content of this pyrometallurgically produced sulphide, this product requires an acid leaching prior to the crucible fusion. This step removes the bulk of the base metals and leaves the precious metals in a concentrated form in the leach residue.

Place the sample weighing up to 60 g, in a 1500-mL beaker and add approximately 25 g of ammonium chloride and 100-200 mL of 12 N hydrochloric acid. Cover the beaker, and heat the contents until the evolution of hydrogen sulphide ceases (about 1 h).

Dilute the sample with an equal volume of distilled water and filter the solution through a Whatman No. 40 filter paper. Should the leach residue appear to exceed 1-3 g, repeat once or twice the hydrochloric acid leaching and filtration steps.

Transfer the final residue to the original filter paper and wash the paper and contents thoroughly with 5% vol/vol hydrochloric acid. Dry the washed residue and paper at ≈110° for about 1 h, and proceed with the usual crucible fusion.

Fusion of Chromite

There is no certified precious metal standard containing a significant amount of chromite available at this time to provide analytical data to support a recommended pretreatment step. However, experience with such materials in CANMET has led to the following procedure for the decomposition of chromite.

Mix the powdered sample with 1.5 times its weight of sodium peroxide, place on a bed of 10 g of silica in a roasting dish, and heat at 700°C with intermittent stirring for about 1 h. Cool, grind the sintered cake and underlying silica together in a mortar, mix with the flux for the crucible fusion, and proceed with the fusion. Subtract the weights of sodium peroxide and silica used from the weights of sodium carbonate and silica contained in the flux charge.

Fusion with Niter for Galena

When a sample of galena, or other sulphide material that contains appreciable quantities of lead, is to be analyzed for precious metal content, a similar roasting step cannot be applied to eliminate the sulphides prior to crucible fusion. The melting point of lead is lower than the temperature of calcining, which would cause the calcine to become viscous and adhere to the roasting dish. In such cases, rather than roasting, some niter (KNO_3) is added to the fusion charge to oxidize the sulphides.

A specific niter charge cannot be given because it would not be applicable to the wide diversity of samples encountered in assaying. The choice of the optimum flux requires much experience in assaying; users of this manual should refer to page 12 for information on this matter.

ASSAY FLUX

Premixed Flux

Although it is theoretically possible to calculate an ideal assay charge for a given ore, the exact composition of an ore is seldom known to the assayer; even if a complete analysis were available, the time required to calculate the assay charge is not warranted. Hence, for simplicity and convenience, this laboratory uses a supply of premixed flux containing the principal ingredients; only the addition of flour and silica is required for fluxing most samples. The composition of the premixed flux is as follows: litharge (PbO) 63%, sodium carbonate (Na_2CO_3) 25%, and borax glass ($Na_2B_4O_7$) 12%.

Flux for Crucible Fusion

A mixture found suitable as a flux for many materials consists of the following; premixed flux (145 g), SiO_2 (10-20 g) (according to silica content of sample), and flour (3-5 g) (the larger quantity for samples high in iron oxide). An additional 30 g of PbO is added to this flux for samples high in copper or nickel, or both. The quantities of flour and silica cannot be specified as they depend on the nature of the samples. Again, experience dictates the choice of the most suitable flux.

DETAILED PROCEDURES

Certain steps in the classical fire-assay procedure for gold and silver are common to many of the methods included in this manual; these steps are shown below to avoid repetition later. Other steps in the assay procedure are described in detail when required.

Crucible Assay Fusion

Blend thoroughly up to 1 assay-ton of powdered sample (pretreat if necessary) with the appropriate flux as described and transfer the whole mixture to a 30-g crucible. Place the crucible in an assay furnace at 1050°C and fuse the contents for about 1 h to produce a lead button weighing 30-45 g. At the completion of the fusion period, pour the highly fluid melt into a conical steel mould and, when cool, separate the button from the slag by tapping with a hammer.

If the lead button contains Cu, Ni, or Co, proceed with the following treatment, otherwise follow the steps described in the appropriate procedure of the classical fire-assay method.

Treatment of Impure Lead Buttons

Scorification

Increase the mass of the lead button from the crucible fusion to approximately 70 g with granulated test lead and transfer to a scorifying dish. Place the scorifier in the furnace and heat at about 1000°C until the molten slag completely covers the lead button. Pour the melt into a conical steel mould, allow to cool, and separate the lead button from the slag by tapping with a hammer. If the button still contains impurities (as indicated by the colour of the slag on the scorifier) repeat this procedure. Continue the analysis as described in the classical fire-assay method.

Litharge soaking

Heat a mixture containing 60 g of litharge (PbO) and 6 g of silica in a 30-g crucible at approximately 900°C until molten. With the aid of tongs, drop the lead fusion button into the melt, maintaining the temperature for about 10 min. Pour the contents into a steel mould, allow to cool, then separate the button from the slag by tapping with a hammer. Continue the analysis as described in the classical fire-assay method.

CLASSICAL FIRE-ASSAY METHOD FOR THE DETERMINATION OF GOLD AND SILVER

Gold and silver are extracted from the sample by lead collection during the crucible fusion. The resultant lead button is subsequently cupelled to form a silver-gold bead which is parted in dilute nitric acid. Gold is determined directly by weight, and silver by weight difference.

APPARATUS AND REAGENTS

Described on page 3.

PROCEDURE

Consult the Preliminary Information and, when required, follow the steps for sample preparation, inquartation, and treatment of impure lead buttons as appropriate in the following procedure.

Fuse the powdered sample with the assay flux as described on page 7. Transfer the resultant lead button to a preheated cupel, and heat at approximately 900°C to absorb all traces of lead oxide by the cupel, leaving a silver-gold bead. Place the bead on a small anvil, clean and flatten, then weigh and record the weight of total precious metals. Transfer the bead to a porcelain parting cup, add approximately 20 mL of 25% vol/vol nitric acid, and heat gently for about 15 min to ensure all the silver has dissolved. Decant the silver nitrate solution and wash the gold residue several times with hot distilled water. Dry on a hot plate the parting cup containing the gold, then anneal the gold by heating the cup over a hot burner flame for about 2 min. Cool and weigh the contents (as pure gold) on a microbalance. Calculate the silver as weight by difference from the total weight of the original bead.

APPLICATION TO OTHER PRODUCTS

Gold Amalgam

Transfer the globule of mercury-gold amalgam to a 400-mL beaker, add 100 mL of 50% vol/vol nitric acid, cover, and heat to dissolve all the mercury (and silver if present). Remove the cover and wash with 10% vol/vol nitric acid, dilute the solution with an equal volume of water and recover the gold residue by filtration through a Whatman No. 41 filter paper (9 cm). Wash the filter paper and beaker several times with 10% vol/vol nitric acid, then transfer the paper containing the gold to a scorifier and dry on the hot plate. Add approximately 50 g of granulated lead as a cover, then scorify at about 1000°C. Cupel the resultant lead button to obtain the pure gold bead for weighing.

Gold Bullion

Weigh duplicate 500-mg samples of the bullion (in the form of chips or drillings) and carefully transfer to a scorifier dish containing about 35 g of granulated lead. Inquart by adding pure silver foil so that the silver-gold ratio will be within the limits of 2:1-3:1, then cover the sample with an additional 30 g of granulated lead and scorify at about 1000°C. Cupel the resultant lead button to obtain a precious metal bead; part in approximately 20 mL of 25% vol/vol nitric acid, decant, and treat again with 50% vol/vol nitric acid to ensure complete silver-gold separation. Wash the gold residue several times with hot distilled water, anneal, and weigh. Report the gold assay in fineness; duplicate results should check within 0.1 parts fineness.

Carry out a proof assay, using high-purity silver and gold in the same proportions by weight as the sample through the above procedure with each set of duplicate samples. Correct the sample results for any loss of gold found in the proof assay.

If the silver content of the gold bullion is required, take a separate 500-mg sample; do not inquart. Transfer to a scorifier, cover with 60 g of test lead, and scorify. Cupel the resultant lead button and weigh the precious metal bead. Determine the weight of silver by subtracting the corrected weight of gold obtained above from the total weight of the precious metal bead and report the silver assay in fineness.

Alternatively, bullion may be assayed for both silver and gold using a single sample. This procedure is especially applicable to routine control analysis.

Gold in Military Braid

Remove, by hand, the very fine lace which holds the braid in place. Weigh duplicate representative portions of the braid, then follow the procedure described for the gold bullion assay, including the recommended silver inquartation. A proof assay is not required.

Analysis of Solutions

The two, principal fire-assay procedures used for the analysis of solutions containing large quantities of gold and silver (g/L) are the lead-tray- and litharge-evaporation methods. The latter is more reliable and accurate and is applicable to solutions of any quantity and character. The lead-tray evaporation method is more convenient and requires little of the analyst's time. This method is confined to concentrated, neutral solutions containing only salts of the precious metals, and where an aliquot of approximately 50 mL is sufficient for analysis. The procedural details of both methods follow.

Lead-tray evaporation

Place the lead-tray on the hot plate, add by pipette up to 50 mL of solution, and evaporate to dryness at a low heat to prevent spattering. Remove the tray from the hot plate, cool, then fold into a compact mass and cupel at

approximately 900°C to produce a precious metal bead. Refer to the classical fire-assay procedure on page 9, for treatment of the bead. Report the result in g/L.

Litharge evaporation

The premixed flux is not used in this evaporation procedure because sodium carbonate and borax glass combine with the solution upon drying to form a hard cake. The residue then is very difficult to remove cleanly from the porcelain dish for blending prior to the crucible fusion.

Transfer an aliquot of sample solution to a porcelain evaporating dish containing 90 g of litharge. Evaporate the mixture on the hot plate at low heat to prevent spattering. When dry, scrape out the residue with the aid of a spatula and brush onto a mixing sheet; add Na_2CO_3 (36 g), $Na_2B_4O_7$ (18 g), SiO_2 (20 g), and flour (3 g). Blend thoroughly, then transfer the mixture to a 30-g crucible and fuse at 1000°C for 1 h to produce a lead button. Refer to the classical fire-assay procedure described on page 9, for further treatment of the lead button in the determination of gold and silver.

Alternate procedure

As an option to the analyst, solutions containing milligram quantities of gold and silver can be determined by atomic absorption spectrophotometry instead of the classical gravimetric procedure. Once the lead fusion button has been obtained by the litharge evaporation method, refer to page 14 under "Procedures" for the determination of gold and silver by AAS.

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ABBREVIATED FIRE-ASSAY ATOMIC-ABSORPTION METHOD FOR THE DETERMINATION OF GOLD AND SILVER

A simplified scheme combining collection by classical fire assay with an atomic-absorption Spectrophotometry finish is applied to the determination of gold and silver (1). The lead button is scorified to approximately 3 g, parted in nitric acid, and the resultant solution is filtered. The filtrate is analyzed for silver by AAS; the residue is dissolved in aqua regia and subsequently analyzed for gold by AAS.

The method eliminates tedious steps associated with the classical finish, such as inquartation, cupellation, parting, removal of particulate matter from the bead, and weighing the bead; thus the possibility of errors and mechanical losses is decreased. Consequently the application of this method to samples with a low content of gold or silver should result in greater accuracy and precision than that expected from the gravimetric finish.

INTERFERENCES

Certain metal impurities are eliminated by calcining (roasting) prior to the crucible fusion. Metals such as copper, nickel, and iron, which could interfere in the AAS finish are eliminated during the crucible fusion and scorification steps. These matters are discussed under "Pretreatment of Samples" on page 6, and "Detailed Procedures" on page 8.

APPARATUS

- Atomic-absorption spectrophotometer.

REAGENTS

- Standard silver and gold solutions. Both of the following concentrations; 100 µg/mL, and 10 µg/mL or 20 µg/mL respectively. Prepare as described on page 4.

- Aqua regia. Mix 3 parts of concentrated hydrochloric acid with 1 part of concentrated nitric acid; prepare freshly as required.

- Cadmium-copper sulphate solution (2). Dissolve 98 g of $CuSO_4 \cdot 5H_2O$ and 57 g of $3CdSO_4 \cdot 8H_2O$ in 500 mL of concentrated hydrochloric acid and 300 mL of distilled water; dilute the resulting solution to 1 L with distilled water.

- Diethylenetriamine, technical grade.

- Lead acetate solution. 5% wt/vol in distilled water.

- Powdered zinc metal. Free of silver and gold.

PREPARATION OF CALIBRATION CURVES FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

Silver Curve

For assay portions containing milligram quantities of silver

To a series of 250-mL beakers containing 3 g of granulated lead, add by buret 1, 3, 6, and 9 mL of the standard 100 µg/mL silver solution. Add 25 mL of 25% vol/vol nitric acid, cover, and heat to dissolve the lead. Cool, wash the cover with 5% vol/vol nitric acid, and, while stirring, cautiously add 2-3 mL of diethylenetriamine to each solution to complex the silver and lead (3). Add 10 mL of concentrated nitric acid, transfer each solution to a 200-mL volumetric flask, and dilute to volume with water. This procedure results in a linear calibration curve in the range 0.5-4.5 µg/mL silver.

Measure absorbance of the solutions by AAS at 328.1 nm in an oxidizing air-acetylene flame.

For assay portions containing microgram quantities of silver

In the same way, take aliquots of 1, 4, 5, and 7 mL of the standard 10 µg/mL silver solution, carry through the previous procedure, and finally dilute to 100 mL. This procedure results in a linear calibration curve in the range 0.1-0.7 µg/mL silver.

Gold Curve

Cadmium-copper sulphate matrix

To a series of 100-mL volumetric flasks add 20 mL of cadmium-copper sulphate solution, and 50 mg of sodium chloride; then by buret add 2, 6, 12, and 15 mL of the standard 20 µg/mL gold solution and dilute to 100 mL with distilled water. This procedure results in a linear calibration curve in the range 0.4-3 µg/mL gold.

Measure the absorbance of the solution by AAS at 242.8 nm, with an oxidizing air-acetylene flame.

Aqua regia matrix

To a series of 200-mL volumetric flasks add 10 mL of aqua regia, then by buret add 1, 3, 5, and 7 mL of the standard 100 µg/mL gold solution and dilute to volume with distilled water. This procedure results in a linear calibration curve in the range 0.5-3.5 µg/mL gold.

Measure the absorbance of the solution by AAS at 242.8 nm, with an oxidizing air-acetylene flame.

PROCEDURE

Pretreat the sample if necessary, and perform the crucible fusion as described on page 9 to obtain a lead button.

Place the lead fusion button in a scorifier and heat at about 1000°C until the slag covers the molten lead. Pour the melt into a conical steel mould, allow to cool, then separate the button from the slag by tapping with a hammer. Increase the button weight to approximately 35 g with granulated test lead and repeat the scorification to obtain a lead button of about 3 g for analysis (Notes 1 and 2).

Determination of Silver

Clean the button of adhering slag, flatten, then cut into pieces with a pair of snips and transfer to a 250-mL beaker. Add 30 mL of 25% vol/vol nitric acid, cover, and heat for about 5 min to dissolve all the lead. Remove the beaker from the hot plate, wash the cover with 5% vol/vol nitric acid, then add very cautiously, with constant stirring, 2-3 mL of diethylenetriamine to complex silver and lead compounds (Note 3). Add 10 mL of concentrated nitric acid to acidify the sample solution, then wash down the sides of the beaker with distilled water. Filter by decantation through a Whatman No. 40 filter paper (9 cm) containing some paper pulp into a 200-mL volumetric flask. Wash the beaker and filter paper thoroughly with hot distilled water, then dilute the filtrate to volume with distilled water. Retain the beaker and filter paper containing the gold.

Measure the absorbance of the resulting solution by AAS using the same conditions as used for the milligram calibration curve. Should the sample solution exceed the concentration range of this curve, remove a suitable aliquot of the sample solution and dilute to volume with 5% vol/vol nitric acid.

When the assay portion contains microgram quantities of silver, filter the sample solution into a 100-mL volumetric flask instead of the 200-mL flask described. Measure the absorbance of the solution by AAS using the microgram curve. Determine the silver content of the sample from the respective calibration curve.

Determination of Gold

When assay portion contains less than 0.1 mg gold (Note 4)

Following the filtration of the sample solution as described above, transfer the filter paper to the original beaker. Add 15 mL of aqua regia, cover and heat slowly until the paper breaks down to a fine pulp; this ensures complete dissolution of the total gold. Remove the cover, wash with 5% vol/vol hydrochloric acid, dilute the gold sample solution with an equal volume of water and filter through a Whatman No. 31 filter paper (9 cm) into a 400-mL beaker. Wash the original beaker and filter paper several times with 5% vol/vol hydrochloric acid. Add 50 mg of sodium chloride to the solution, and

evaporate slowly to near dryness. Do not heat the solution strongly or allow the sample to bake dry, otherwise metallic gold could be formed. Add 10 mL of concentrated hydrochloric acid to the salts, and again evaporate to near dryness to remove most of the nitric acid. The hydrochloric acid treatment and subsequent evaporation is repeated twice.

Cool the sample and add 5 mL of cadmium-copper sulphate solution to eliminate possible interferences from small amounts of lead that may have been retained with the gold after parting the lead button. Transfer the solution to a 25-mL volumetric flask and dilute to volume with distilled water.

Measure the absorbance of the resulting solution by AAS using the same conditions as for the cadmium-copper calibration curve. Determine the gold content of the sample from the calibration curve.

When assay portion contains 0.1 mg or more gold (Note 4)

After treatment of the gold residue with 15 mL of aqua regia as described above, filter the resultant sample solution through a Whatman No. 31 paper into a 200-mL volumetric flask instead of a 400-mL beaker. Wash the filter paper and beaker several times with hot 5% vol/vol hydrochloric acid, then dilute the sample to volume with distilled water.

Measure the absorbance of the resulting solution by AAS and determine the gold content of the sample from the aqua regia calibration curve.

Notes

1. In routine control analysis where the mineralogical composition of the samples does not vary significantly, the weight of the lead button could be controlled at 25-35 g, thus eliminating the need for a second scorification. At CANMET we use the 7.5-cm diameter Denver clay scorifier that reduces a 35-g lead button to 2-3 g in a single scorification. For fusion buttons weighing under 35 g, the difference in weight is made up with granulated lead.

2. In the analysis of lead buttons weighing more than 3-4 g, precipitation of lead salts with diethylenetriamine occurs, which results in low precious metal values as a result of occlusion. Also, blockage of the AA nebulizer occurs under these conditions.

3. Treatment of the sample solution with diethylenetriamine is a modification of the procedure by Greaves (3). Elements that precipitate as hydrous oxides under these conditions are, in general, those that form precipitates in a slightly ammoniacal media.

4. When the assay portion contains 0.1 mg or more gold, the insoluble gold residue obtained after dissolving the 2-3 g lead button is visible to the analyst. When the assay portion contains gold at the lower milligram level (<0.1) the resultant gold residue is so finely divided, that the gold cannot be detected visually.

APPLICATION TO CYANIDE SOLUTIONS USING ZINC-LEAD PRECIPITATION

In the zinc-lead precipitation method, the gold and silver are precipitated and collected in a lead sponge. The lead sponge is then scorified and the gold and silver subsequently determined by AAS. This method is suitable for large or small assay portions, and is one of the most popular for low-grade solutions.

Transfer the assay portion of solution to a 400-mL beaker, add 100 mL of distilled water and 40 mL of a 5% vol/vol lead acetate solution. Heat the sample solution to near boiling, then add slowly with intermittent stirring 1 g of zinc powder, cover, and continue heating for about 15 min to ensure complete reduction of the lead. Slowly add with stirring 30 mL of 1:1 hydrochloric acid, cover and continue heating a few minutes to dissolve excess zinc. Allow the solution to cool.

Filter the solution through a Whatman No. 40 filter paper, and transfer the lead to the paper. Wash the paper and lead several times with hot distilled water then place in a scorifier and dry on the hot plate. Add 35 g of granulated lead to the sample and scorify to produce a 2-3 g lead button. Follow the procedure on page 14 for the determination of silver and gold by AA. Report the results in mg/L.

In addition to this method, a direct chemical procedure for the determination of gold only in cyanide solutions is described on page 25 of this manual.

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FIRE-ASSAY WET-CHEMICAL METHOD FOR THE DETERMINATION OF SILVER, GOLD, PLATINUM, AND PALLADIUM

This method (1) is an extension, to include palladium and platinum, of the abbreviated fire-assay atomic-absorption method for the determination of gold and silver in ores and concentrates (2). After parting the 3-g lead button with dilute nitric acid, and separating the solution from the residue, the platinum and palladium in the solution are precipitated by the addition of stannous chloride using tellurium as a collector (3). The resulting precipitate is combined with the gold residue, is dissolved in aqua regia and the solution is analyzed for gold, palladium, and platinum by AAS. Silver is determined in the original solution by AAS before the reduction step. A flow chart of the analytical scheme for the determination of silver, gold, palladium, and platinum in a powdered sample is shown in Figure 2.

INTERFERENCES

Refer to "Pretreatment of Samples" on page 6, describing the procedures for removing certain metal interferences. Inter-element interference in the AAS determination for gold, platinum, and palladium is avoided by adding a buffering solution of cadmium-copper sulphate to both the sample and calibration solution. There is no interference from platinum and palladium in the silver determination by AAS.

APPARATUS

- Atomic-absorption spectrophotometer. A Techtron Model AA-5 is currently used in CANMET, but any instrument would be satisfactory provided it is capable of sufficient sensitivity for the precious metal concentration ranges used. An instrument with curve-correction capability would be especially helpful for the platinum determinations as the platinum response is usually not linear.

REAGENTS

- 1 M stannous chloride solution (2 M HCl). Dissolve 22.5 g of $SnCl_2 \cdot 2H_2O$ in 16 mL of concentrated hydrochloric acid. Cover, heat gently until the solution is clear, then dilute to 100 mL with distilled water. The stannous chloride should be of the highest purity, and prepared fresh as required.

- Tellurium powder, reagent grade.

- Diethylenetriamine, technical grade.

- Mixed cadmium-copper sulphate solution (4). Dissolve 98 g of $CuSO_4 \cdot 5H_2O$ and 57 g of $3CdSO_4 \cdot 8H_2O$ in 500 mL of concentrated hydrochloric acid and 300 mL of distilled water, and dilute to 1 L with distilled water.

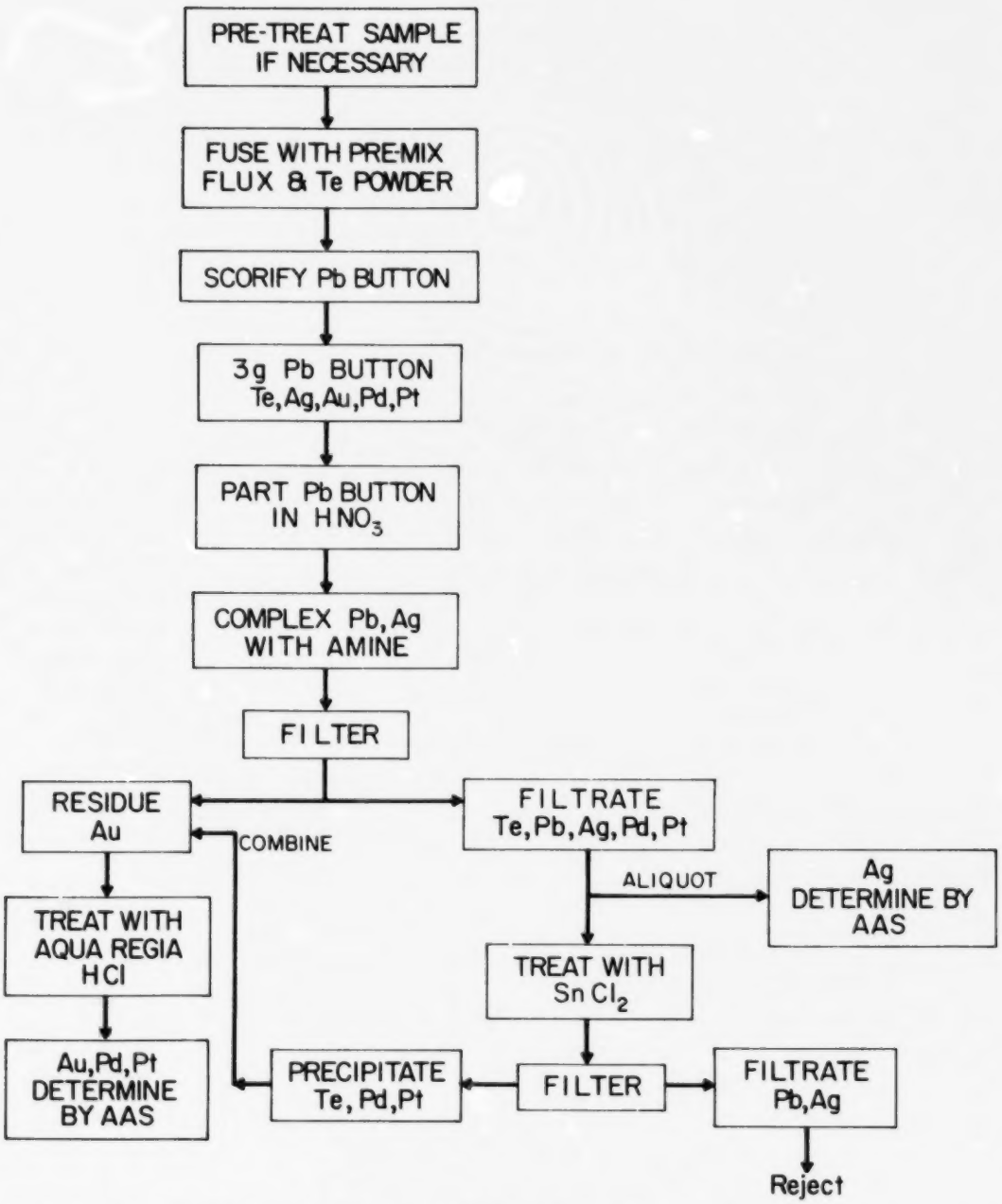

Figure 2. ANALYTICAL SCHEME FOR Ag, Au, Pd, Pt

- Aqua regia. Mix 3 parts of concentrated hydrochloric acid with 1 part of concentrated nitric acid; prepare fresh as required.

- Flux for crucible fusion. Use the recommended portions as described under "Assay Flux" on page 7, and add 15-18 mg of tellurium powder.

- Standard silver, gold, palladium, and platinum solutions. Prepare as described on page 4.

PREPARATION OF CALIBRATION CURVES FOR AAS

Silver and Gold Curves

Prepare linear AAS calibration curves in the range 0.5-4.5 µg/mL and 0.1-0.7 µg/mL silver, and 0.4-3 µg/mL gold, as previously described on page 13.

Palladium Curve

Prepare a series of palladium standards from the 20 µg/mL palladium stock solution by following the procedure used for the preparation of the gold standards on page 13, which results in a linear calibration curve in the range 0.4-3.0 µg/mL palladium.

Measure the absorbance of the solutions by AAS at 244.8 nm, in an oxidizing air-acetylene flame.

Platinum Calibration Solutions

To a series of 100-mL volumetric flasks add 20 mL of cadmium-copper sulphate solution, and 50 mg of sodium chloride; then by buret add 4, 6, 8, 10, and 12 mL of the standard 20 µg/mL platinum stock solution and dilute to 100 mL with distilled water. This procedure provides calibration standards in the range 0.8-2.4 µg/mL.

Measure the absorbance of the calibration solutions by AAS at 266.0 nm, in an oxidizing air-acetylene flame. Because the platinum AAS response is not linear, a calibration curve is not prepared.

PROCEDURE

Pretreat the sample, if necessary, and perform the crucible fusion as described in detail in the "Preliminary Information" on page 8, to obtain a lead button.

Transfer the lead button to a scorifying dish and proceed to obtain a 3-g lead button for analysis, as described in the previous method on page 14 (Notes 1 and 2).

Silver Determination

Clean the button of adhering slag, flatten, then cut into pieces with a pair of snips and transfer to a 400-mL beaker. Add 30 mL of 25% vol/vol nitric acid, cover, and heat for about 5 min to dissolve the lead. Cool the sample, wash the cover with 5% vol/vol nitric acid, and add cautiously, with constant stirring, 5 mL of diethylenetriamine to complex lead and silver compounds (Note 3). Add 10 mL of concentrated nitric acid to acidity the sample solution, wash down the sides of the beaker with distilled water, then filter through a Whatman No. 40 filter paper (9 cm) containing some paper pulp into a 200-mL volumetric flask. Wash the beaker and filter paper thoroughly with hot distilled water, and dilute the filtrate, containing silver, palladium, and platinum, to volume with distilled water. Retain the beaker and filter paper containing the gold.

Remove a 10-mL aliquot of the filtrate and transfer to a clean dry 25-mL volumetric flask, and measure the absorbance by AAS at 328.1 nm in an oxidizing air-acetylene flame. For milligram quantities, dilute an aliquot to an appropriate volume with 5% vol/vol nitric acid. Determine the silver content of the sample from the calibration curve.

Gold, Palladium, and Platinum Determination

Transfer the sample solution remaining in the 200-mL volumetric flask to the original 400-mL beaker, cover, and heat to 80°C. Remove the sample from the hot plate, and add exactly 15 mL of stannous chloride solution dropwise by buret (2 drops per second) with constant stirring to coprecipitate platinum and palladium with the tellurium. Cover, then allow the precipitate to coagulate and settle (about 1 h), then filter the solution through the original filter paper containing the gold. Wash the paper and beaker several times with hot distilled water, then discard the filtrate containing the lead and silver. Transfer the paper and contents back to the original beaker, wash down the sides with 15-20 mL of freshly prepared aqua regia, cover, and heat slowly until the filter paper breaks down to a fine pulp, to ensure complete dissolution of the precious metals. Wash the cover with distilled water, and dilute the sample solution with an equal volume of water and filter through a Whatman No. 31 filter paper into a 400-mL beaker. Wash the paper several times with hot 5% vol/vol hydrochloric acid, add 50 mg of sodium chloride to the solution to help prevent the formation of elemental gold, and evaporate slowly to near dryness. Dissolve the salts in 10 mL of concentrated hydrochloric acid and evaporate again to near dryness to remove most of the nitric acid. Repeat the hydrochloric acid treatment twice with subsequent evaporations.

Cool the sample, add 5 mL of cadmium-copper sulphate solution and transfer the mixture to a 25-mL volumetric flask and dilute to volume with distilled water.

Measure, by AAS, the gold, palladium, and platinum absorbance of the resulting solution at 242.8, 244.8, and 266.0 nm, respectively. Determine the gold and palladium contents of the sample from their calibration curves. Determine the

platinum content of the sample, by reading the sample solution between platinum standards of slightly higher and lower concentrations. Make allowance in the palladium and platinum calculation for the 10-mL portion of sample removed from the 200-mL flask for the silver determination.

For milligram amounts of one or more of gold, palladium, or platinum, take an aliquot from the 25-mL volumetric flask, add additional cadmium-copper sulphate solution to maintain a 20% vol/vol concentration, and dilute to the required volume with distilled water. Determine the precious metal content of the sample by AAS.

Special note

In the application of this procedure, it is very important that the resultant 3-g lead button for analysis contains no copper. Copper, when present, will precipitate with the tellurium during the stannous chloride reduction step, which results in obtaining a very fine precipitate which remains in suspension, thus making the subsequent filtering step very difficult.

Notes

1. In routine control analysis where the mineralogical composition of the samples does not vary significantly, the weight of the lead button could be controlled at 25-35 g, thus eliminating the need for a second scorification. At CANMET we use the 7.5-cm diameter Denver clay scorifier, which reduces a 35-g lead button to 2-3 g in a single scorification. For fusion buttons weighing under 35 g, the difference in weight is made up with granulated lead.

2. In the analysis of lead buttons weighing more than 3-4 g, precipitation of lead salts with diethylenetriamine occurs, which results in low precious metal values because of occlusion. Also, blockage of the AA nebulizer occurs under these conditions.

3. Treatment of the sample solution with diethylenetriamine is a modification of the procedure by Greaves. Elements that precipitate as hydrous oxides under these conditions are, in general, those that form precipitates in a slightly ammoniacal media.

APPLICATION TO PRECIOUS METAL ALLOYS

Dental Alloy

This alloy usually contains about 80-90% total precious metals, with gold being the major constituent, followed by silver and palladium. The platinum content is about 1%.

Procedure

Weigh, in duplicate, approximately 100 mg of the dental alloy (in the form of chips) and transfer to a scorifier. Add 15-18 mg of tellurium powder and 35 g of test lead and heat in the furnace at 1000°C until the molten slag covers the lead. Pour the melt into a conical steel mould, allow to cool, then separate and clean the resultant lead button from the slag by tapping with a hammer. Flatten the lead button, then cut into pieces with a pair of snips and transfer to a 400-mL beaker for the determination of silver, gold, palladium, and platinum.

Gold determination

Because gold is the major constituent and could range up to 75% of the alloy, it would be more accurate to determine it by the standard gravimetric procedure than by AAS.

Part the 3-g lead button obtained by the procedure above in dilute nitric acid, then follow the procedure for the determination of silver as described on page 21. Ensure that the gold residue obtained after parting is quantitatively transferred to the filter paper and wash the paper several times with hot distilled water. Transfer the paper plus gold to a scorifier, dry, then add about 50 g of test lead as a cover, and scorify to produce a lead button. Cupel the button, then clean and weigh the resultant pure gold bead.

Silver determination

Remove a 10-mL aliquot of the 200 mL of filtrate obtained after the above gold separation, then follow the procedure on page 21 for the silver determination by AAS.

Palladium and platinum determination

Follow the procedure on page 21 for the recovery and determination of platinum and palladium by AAS in the 200 mL of filtrate.

Other Alloys

The procedure described for the analysis of dental alloy would be suitable also for the determination of platinum or palladium, or both, in most jewellers' scrap and sweeps.

For an alloy containing gold or silver, or both, and no other precious metal the classical scorification assay method is recommended. Cover the 100-mg alloy sample with 50 g of test lead and scorify to produce a lead button. Follow the remaining steps of the classical assay procedure on page 9 for the gold and silver determination.

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DETERMINATION OF GOLD IN CYANIDE SOLUTIONS BY SOLVENT EXTRACTION ATOMIC-ABSORPTION SPECTROPHOTOMETRY

Two procedures are presented for the determination of gold in cyanide solutions by atomic absorption: direct extraction of the gold into methyl isobutyl ketone (MIBK), and evaporation of a cyanide solution prior to gold extraction into MIBK. In the direct procedure (1), the monovalent gold in the cyanide solution is oxidized to the trivalent state and then concentrated by solvent extraction prior to determination by atomic absorption. In the cyanide-evaporation procedure (2), a sample of the cyanide solution is evaporated to dryness, then treated with aqua regia and diluted with water. Gold is then extracted and determined by atomic absorption.

The direct procedure reduces significantly the time required for a gold determination by eliminating the sample evaporation and digestion steps associated with the alternative procedure. Therefore, the application of the direct procedure is preferable for routine control analysis, where the gold concentration of the sample solution can be determined on a maximum sample portion of 60 mL. For barren solutions that require a considerably larger sample, the evaporation procedure can be used.

EXTRACTION OF GOLD WITH METHYL ISOBUTYL KETONE

Methyl isobutyl ketone has been used extensively to preconcentrate gold when it is to be determined by AA when the sensitivity is too low for determination in aqueous solution. Although this reagent has excellent flame characteristics, there are problems associated with its use (3,4). Volume changes of the solvent occur during extraction, caused by the solubility of MIBK in the aqueous phase and by the solubility of acid or water in the MIBK phase. These volume changes can be minimized by using MIBK equilibrated with acid for the gold extraction, and acid solutions equilibrated with MIBK for scrubbing the solvent prior to the atomic-absorption determination.

Moreover, when gold is extracted into MIBK from a hydrochloric or hydrobromic acid medium, metals such as copper, iron, and zinc, if present in the sample solution, are also extracted. Such contaminants may cause erroneous atomic-absorption results for gold, or nebulizer blockage, or both. Scrubbing of the ketone phase with equilibrated 5% vol/vol hydrochloric acid or hydrobromic acid removes these contaminants effectively.

APPARATUS

- Atomic-absorption spectrophotometer. A Varian Model AA-6 has been used in CANMET, operated with the following parameters.

  wavelength 242.8 nm
  lamp current 14 mA
  spectral band pass 300 microns
  flame: air-acetylene, adjusted to maintain a low blue flame while aspirating equilibrated MIBK

• Separatory funnels. 125-, 250-, and 500-mL capacity.

REAGENTS

• Aqua regia. Mix 3 parts of concentrated hydrochloric acid with 1 part concentrated nitric acid; prepare fresh as required.

• Equilibrated 5% vol/vol hydrochloric acid. Shake approximately 150 mL of the acid solution with about 15 mL of MIBK for 1 min in a separatory funnel, allow to settle, then collect the acid phase.

• Equilibrated 5% vol/vol hydrobromic acid. Prepare the same as for the hydrochloric acid.

• MIBK, analytical reagent grade.

• Equilibrated MIBK. Shake the MIBK with an equal volume of 20% vol/vol hydrochloric acid for 1 min in a separatory funnel, allow to settle, then collect the solvent phase.

• Hydrobromic acid, 48% reagent grade.

• Bromine water, saturated solution.

Standard Gold Solution

Prepare a standard gold solution, 100 μg/mL and 5 μg/mL in 10% vol/vol kydrochloric acid, as described on page 4. From this stock solution, prepare a 5 μg/mL gold stock solution by diluting a 5-mL aliquot and 9.5 mL of concentrated hydrochloric acid to 100 mL with distilled water.

Preparation of Calibration Solutions

Prepare a series of calibration solutions by dispensing by buret into 125-mL separatory funnels appropriate quantities of gold from the 5-μg/mL stock solution to cover the range 0-2.0 μg/mL, to provide standards of slightly higher and slightly lower gold concentrations than the samples. To each funnel, add 5 mL of aqua regia and dilute to approximately 40 mL with distilled water. By pipette, add 10 mL of equilibrated MIBK and shake the mixture vigorously for 1 min. Allow to settle, then remove and discard the aqueous phase. Scrub the ketone fraction by shaking for a few seconds with 15 mL of 5% vol/vol equilibrated hydrochloric acid, and discard the aqueous washings. Transfer the MIBK phase into a 25-mL volumetric flask, dilute to volume with equilibrated MIBK, stopper, and retain. Calibration solutions are prepared for each series of samples analyzed.

PROCEDURE

Direct Gold Extraction From Cyanide Solutions

Microgram quantities of gold

Transfer up to 60 mL of the gold cyanide solution to a 125-mL separatory funnel, add 5 drops of bromine water and mix. Working under a well-ventilated hood, add 5 mL of 48% hdyrobromic acid and allow the mixture to stand a few minutes for the evolution of hydrogen cyanide gas. By pipette, add 10 mL of equilibrated MIBK and shake for 1 min. Allow to settle, remove, and discard the aqueous phase, and scrub the ketone phase with 15 mL of 5% vol/vol equilibrated hydrobromic acid. If the ketone phase is coloured, repeat the acid wash until the solvent is clear. Remove and discard the aqueous phase, transfer the MIBK phase into a 25-mL volumetric flask and dilute to volume with equilibrated MIBK.

Measure the absorbance of the ketone phase along with the reference calibration standards by AAS, using equilibrated MIBK as a reference blank. Calculate and report the gold concentration of the cyanide solution in µg/mL.

Milligram quantities of gold

For the determination of milligram quantities of gold, prepare a series of calibration solutions in the range 0-10.0 µg/mL, as described above, making use of the 100 µg/mL gold stock solution. Extract the gold from the calibration solutions and sample with two 10-mL portions of the equilibrated MIBK. After this double extraction, remove and discard the aqueous phase. Scrub the ketone fraction by shaking for a few seconds with 15 mL of 5% vol/vol equilibrated hydrochloric acid, and discard the aqueous washing. Transfer the ketone phase into 25-mL volumetric flasks, and dilute to volume with equilibrated MIBK.

Measure the absorbance of the ketone phase along with the reference calibration standards by AAS, and calculate and report the gold concentration of the cyanide solution in mg/L. If necessary, turn the burner to a slight angle to reduce the sensitivity.

Gold Cyanide-Evaporation Procedure (Barren Solutions)

Transfer a measured volume (100-200 mL) of the cyanide solution to a 400-mL beaker and, in a well-vented hood, slowly evaporate to dryness to prevent spattering. Cool, wash down the sides of the beaker with 10-15 mL of aqua regia, cover and heat slowly to dissolve and oxidize the gold to the trivalent state. Cool, wash down the sides of the beaker with distilled water, transfer to a 125-mL separatory funnel, and dilute to about 40 mL with distilled water.

If any insoluble matter remains after the acid treatment of the sample, filter the mixture through a Whatman No. 31 filter paper into the 125-mL separatory funnel and wash the beaker and paper several times with 5% vol/vol hydrochloric acid.

Extract the gold using equilibrated MIBK, following the procedure described above for the preparation of the calibration solutions.

Measure the absorbance of the ketone phase along with the calibration solutions by AAS, using equilibrated MIBK as a reference blank. Calculate and report the gold concentration of the cyanide solution in µg/mL.

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APPENDIX

ACCURACY AND PRECISION

Tables A-1 and A-2 demonstrate the accuracy and precision obtained at CANMET, of two of the analytical methods described in this manual, by showing their application to a number of international certified reference materials.

The two analytical methods used to provide the CANMET results in Tables A-1 and A-2 are an abbreviated fire-assay atomic-absorption method for the determination of gold and silver, and a fire-assay wet-chemical method for the determination of palladium, platinum, gold, and silver. The procedural details for both methods are found on pages 12 and 18 respectively.

The precious metal results obtained from both methods are of good precision within themselves and, in addition, show good agreement with the accepted certified or recommended values for the reference materials.

The certified values in turn originate from values supplied by analysts from a number of independent laboratories, and, collectively, represent results from a wide variety of analytical methods.

The South African reference Pt-Pd Ore was prepared by the National Institute for Metallurgy of South Africa. The other five reference materials were prepared by the Canadian Certified Reference Materials Project. The reference numbers in the tables refer to the publication giving details of the preparation and properties of the reference material.

Table A-1: Application of the fire-assay atomic-absorption method to certified reference materials

Sample (ref)	Sample wt, g	Element	Mean found ppm*	Std dev ppm	Relative std dev %	Certified value, ppm
Silver ore KC-1 (1)	14.58	Ag	1113	28.9	2.6	1138
Gold ore MA-1 (2)	14.58	Au	17.9	0.32	1.8	17.8
Flotation concentrate PTC-1 (3)	14.58	Ag	5.75	0.24	3.1	5.80
		Au	0.62	0.05	8.6	0.65
South African ore (4)	14.58	Ag	0.46	0.03	7.2	0.42
		Au	0.32	0.02	5.2	0.31

Concentration of base-metals in the sulphide reference materials: KC-1: Pb-6.98%; Zn-20.3%; S-28.0%; PTC-1: Cu-5.16%; Ni-9.42%; S-23.5%; Fe-26.9%.

**CANMET results.*

Table A-2: Application of the fire-assay wet-chemical method to certified reference materials

Sample (ref)	Sample wt., g	Element	Mean found, ppm*	Std dev ppm	Certified values and 95% confidence intervals	
Magnetic concentrate PTA-1 (5)	14.58	Pt	3.20	0.11	3.05	(2.92-3.16)
Flotation concentrate PTC-1 (3)	14.58	Ag	6.0	0.23	5.8	(5.5-6.2)
		Au	0.65	0.05	0.65	(0.55-0.72)
		Pd	12.3	0.29	12.7	(12.0-13.0)
		Pt	2.9	0.17	3.0	(2.8-3.2)
Cu-Ni matte PTM-1 (6)	7.29	Ag	68.9	1.42	66.0	(59.0-73.0)
		Au	1.7	0.09	1.8	(1.6-1.9)
		Pd	7.8	0.30	8.1	(7.4-8.8)
		Pt	5.2	0.48	5.8	(5.5-6.2)
South African Pt-Pd ore (4)	29.17	Ag	0.47	0.02	0.42	(0.38-0.46)
		Au	0.37	0.03	0.31	(0.30-0.33)
		Pd	1.51	0.03	1.53	(1.50-1.56)
		Pt	3.74	0.10	3.74	(3.70-3.79)

Concentration of base metals in sulphide reference material PTM-1: Cu-30.24%; Ni-44.75%; Fe-1.58%; S-21.6%.

**Based on five replicate determinations in CANMET laboratory.*

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